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Ionization and fragmentation of Bi microclusters by electron impact

R. E. Walstedt and R. F. Bell
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
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Results are presented for an electron-impact ionization study of Bi microclusters ranging in size from one to thirty-eight atoms. By comparing results from two different cluster source conditions, we identify a clear onset for fragmentation in the vicinity of 10.5 eV. This is below the threshold for double ionization, yet well above the first ionization thresholds. The latter thresholds have been found to be almost universally double and are quite sharp, suggesting unique structures for each cluster size. The first threshold energies vary with size in a manner consistent with the classical metal-sphere model.

In recent years several techniques have been developed to generate beams of small metallic clusters,[1-6] opening interesting approaches to the study of how metallic behavior evolves from the properties of small aggregates. Typically, clusters have been ionized for subsequent mass spectrometry by electron impact[2,3] or photoionization[1,4-6] methods, leading to estimates of appearance potentials (AP's) and cluster size distributions. While a wealth of new data has been obtained in this fashion, the interpretation of such data is often complicated by multiple thresholds for single ionization[7] and cluster-fragmentation effects.[8-10] These effects, interesting in their own right, are difficult to identify and distinguish.

In this Rapid Communication we present results from an investigation of Bi microclusters having from one to thirty-eight atoms. Ionization is accomplished by electron impact using a calibrated electron gun. By comparing data obtained with different methods of cluster generation, we have been able to show that the onset of fragmentation is several eV above a typical cluster-ion AP, yet well below the threshold for double ionization.[11] Furthermore, we find sharply defined double thresholds, spaced by only 1–2 eV, for the intrinsic AP curves throughout the range of cluster sizes studied. These multiple ionization thresholds have been examined in detail and are reported here for the first time for metallic clusters.

To obtain accurate AP values, it was necessary to scan electron energies over a range of just a few eV in the vicinity of the first onset. At such low energies one finds a cluster intensity distribution, shown in Fig. 1 for an electron energy of 9.8 eV, which is strikingly different from data reported for higher electron energies[12] in that the intensity declines rather slowly with cluster size.[13] The relative intensity of neighboring peaks is, however, similar to that in Ref. 12, i.e., is unchanged by extensive fragmentation.

The cluster distribution in Fig. 1 was generated by means of the He-gas condensation method developed by Sattler and co-workers[2,14] AP data were also taken under simple high-vacuum evaporation conditions, yielding only the clusters $N=1$–4 with relative intensities shown in the inset to Fig. 1. All AP curves were obtained with the retarding-potential-difference method[15] using, however, a high-current electron gun ($\sim 25\ \mu$A/V) with a square-wave amplitude of 1.0 V on the control element. This setup was found to yield good energy resolution (see Fig. 2) with, however, a negative shift of ~ 3 eV. By studying the monomer AP's for In, Pb, Bi, and Cd (Ref. 16) and assuming spectroscopic ionization potentials, it was established that this shift is constant over a range of electron energies of at least several eV. The Bi monomer AP (Fig. 2) was used to monitor the shift on an alternate-day basis. It was found that the shift is stable over a period of a few weeks without renewing the e-gun electrodes and could be established to within 0.1 eV for calibration purposes.

For our fragmentation study the trimer and tetramer are key particles, because they alone could be observed under both vacuum and gas condensation source conditions. Tetramer AP data taken with both types of cluster source are compared in Fig. 3, where they have been scaled to coincide at energies within ~ 3 eV of the AP. Above electron energies $E \sim 10.5$ eV the gas condensation intensity of Bi_4^+ is seen to rise above and diverge from the vacuum data. Since all conditions are essentially identical except for the cluster size distribution, and since the vacuum source has no clusters larger than Bi_4, the divergence of intensities in Fig. 3 can only be attributed to Bi_4^+ ions produced by fragmentation of larger clusters, $Bi_n + e^- \rightarrow Bi_{n-4} + Bi_4^+ + 2e^-$. The dissociation energy threshold for such processes is thus $E_{dis} \gtrsim 3$ eV. Some evidence has been given[8,9] for fragmentation of Bi_4 in this energy range. We only note that the effect displayed in Fig. 3 is independent of Bi_4 fragmentation.

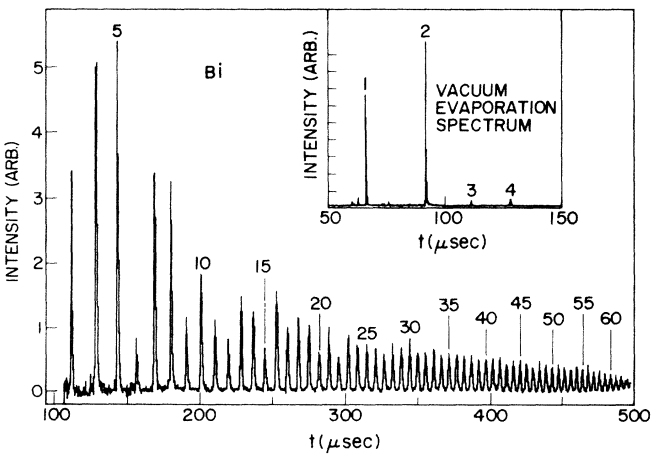

FIG. 1. Differential intensity spectrum of Bi clusters from the gas condensation source obtained with electrons of nominal energy 9.8 eV. Inset shows the cluster distribution obtained with high-vacuum evaporation.

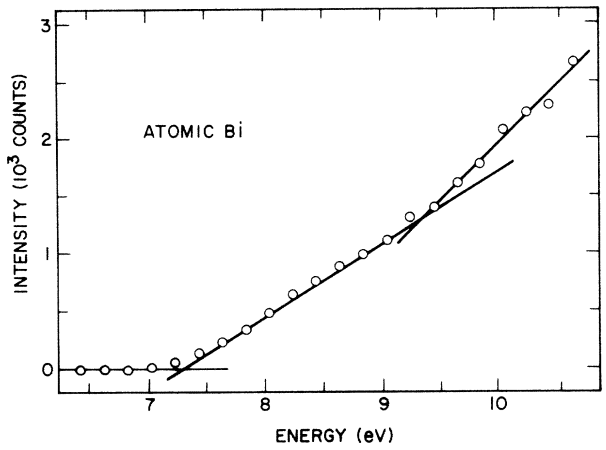

FIG. 2. Intensity vs electron energy for atomic Bi, showing near-linear onset region and extrapolation to base line used to calibrate electron energy shift.

Results similar to Fig. 3 have also been obtained for the trimer.

The foregoing interpretation is corroborated by the behavior of AP curves for larger clusters. For virtually every cluster size represented in Fig. 1 there is a break or other feature in the AP curve at 11.5 ± 1 V. For $N < 20$ the curves mostly turn upward as fragments cascade downward in the size spectrum. Above $N = 25$ almost all AP curves flatten in an apparent loss of intensity from fragmentation. As examples we present in Fig. 4 the AP curves for $N = 6$ and $N = 33$. Above initial double thresholds these data show an upturn (a) and flattening (b), which are typical for their size range. We conclude that a substantial incidence of fragmentation sets in at electron energies of

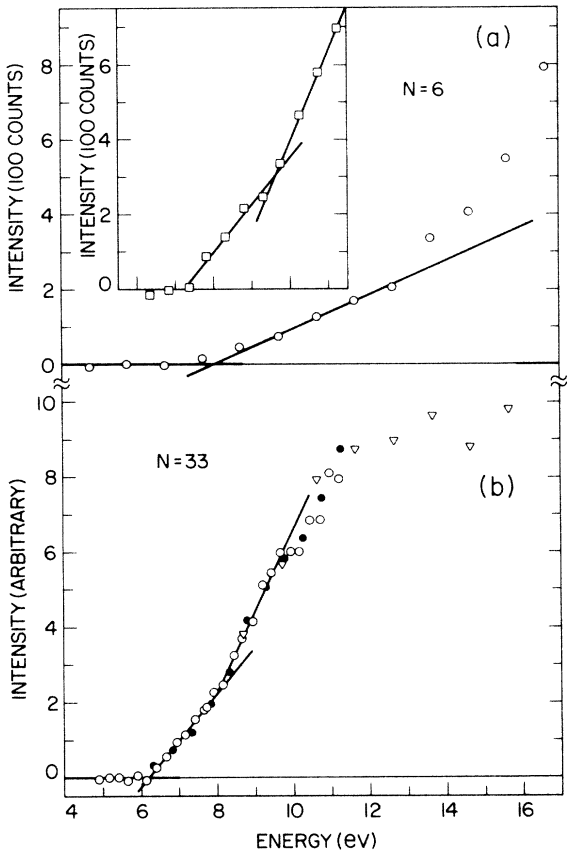

FIG. 4. (a) Double onset threshold (inset) and eventual upward break at $E \sim 12$ V attributed to fragments from larger clusters for $N = 6$ atoms. (b) Similar data to that above for $N = 33$ atoms. Squares and circles are separate data runs spliced together. Flattening above $E \sim 11$ eV is attributed to loss from fragmentation.

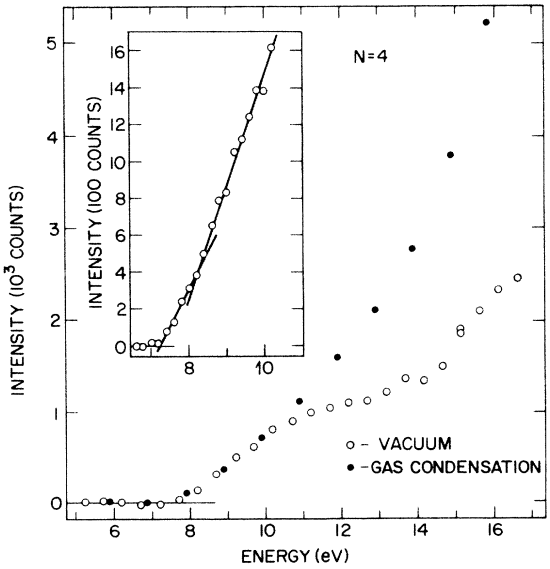

FIG. 3. Intensity vs electron energy for tetramer ions showing a comparison between vacuum data and gas condensation data (Fig. 1) which have been scaled to coincide near the onset. The divergence at higher energies is attributed to fragments from the ionization process of larger clusters. Inset shows details of double onset threshold from vacuum data.

~ 10.5 eV and above, and is especially important for clusters of $N = 20$ atoms and larger. This energy threshold is somewhat lower than that suggested for the case of Sb microclusters.[10]

The double onset threshold seen in Fig. 3 (inset) and in Figs. 4(a) and 4(b) is a general feature observed in nearly all the AP curves investigated, having presumably nothing to do with fragmentation onsets occurring at higher energies. Measured threshold energies for clusters up to $N = 38$ atoms in size are displayed in Fig. 5. The values shown were drawn from two independent bodies of data. A few are omitted because of inconsistent results. In a number of cases ($N = 9$, 10, 16, and 35) the initial onset was rounded, apparently by structure not resolved in the present study. At least two ionization thresholds were observed in every case except for $N = 22$ and 27, where the double thresholds are either absent or unresolved. Apart from these isolated lapses, one observes a marked uniformity in the interval between thresholds for $N > 10$. This interval is plotted for 25 cases at the bottom of Fig. 5, exhibiting a mean value of 1.5 eV with a standard deviation of 0.2 eV, which may be attributed to experimental error.

For monomers and dimers, double ionization thresholds have been attributed to sharp excited energy levels of the final-state ions,[7] a mechanism unlikely to hold for larger metallic aggregates. It is tempting to attribute the second

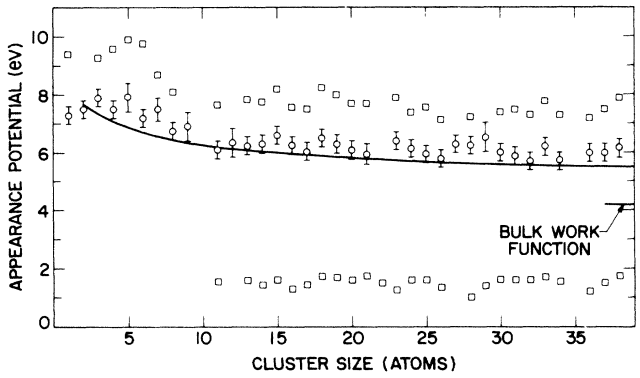

FIG. 5. Plot of measured first and second thresholds in AP curves as a function of cluster size. The solid line is the model curve [Eq. (1)] as described in text. The interval between first and second thresholds for clusters greater than ten atoms is plotted at the bottom (squares).

threshold for Bi_n^+ to the process $Bi_{n+1}+e^- \rightarrow Bi_n^+ + Bi + 2e^-$, since the added dissociation energy required for $Bi_{n+1} \rightarrow Bi_n + Bi$ could become nearly constant as n gets larger. However, such a process would also occasion a downward break in the intensity curve for Bi_{n+1}^+, smearing and weakening its second break point. Since the second thresholds are generally quite distinct (e.g., Fig. 4) this mechanism is apparently absent. Beyond this, one can only speculate that the second thresholds arise out of electronic energy-level structure below the Fermi surface.

We note two other points about the threshold results. The sharpness of the ionization thresholds observed throughout the mass range studied suggests either that the ionization potential (IP) for a given size of cluster is only weakly dependent on its geometry or that these cluster geometries are unique. It is also noteworthy that the odd-even alternation effects observed in photoionization studies of the alkali metals[1,17] and of copper[4] are largely absent here.

Finally, it is interesting to compare the observed variation in initial onset energies from Fig. 5 with available theoretical models of cluster ionization potentials.[1,18-23] The classical metallic-sphere model gives an expression for the IP given by[18]

$$E_i = \phi_{\text{bulk}} + 3e^2/8R \quad , \tag{1}$$

where ϕ_{bulk} is the bulk work function and R is the radius of the sphere. Equation (1) is obtained by considering the charge attraction effect and change in image potential which occur for a finite spherical specimen.[24] In addition, a number of jellium model calculations have been carried out using the density functional formalism, giving electrostatic energy correction terms which are either slightly smaller[19,23] or larger[21,22] than that in Eq. (1). We compare Eq. (1) with the Bi data in Fig. 5 (solid line), assuming the bulk density to estimate R and $\phi_{\text{bulk}} = 4.2$ eV.[25] The data lie above the resulting curve, but only marginally so. This effect could have many possible explanations, including an expected shrinkage of interatomic spacing below bulk values for small clusters. Fluctuations about a smoothly decaying value of the IP are seen to be far less pronounced than the shell structure models[20,23] predict. It is interesting to note that results for the alkali metals[1,17] and for Pb (Ref. 3) are also in reasonable agreement with Eq. (1), whereas transition-metal cluster IP's appear to follow a much smaller correction term.[26] A more detailed account of these studies will be published elsewhere.

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